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To: Interested Parties

Subject: Guidance for Petroleum Hydrocarbon Analysis

Background

The Petroleum Hydrocarbon Methods Committee, which convenes at the Hazardous Materials Laboratory, comprises scientists from state and local agencies, environmental laboratories, consulting firms, and the petroleum industry. The purpose of this committee is to offer guidance on the best available techniques and methods for assessing petroleum contamination in the environment. The committee is a forum for participants to share information, and its role is strictly advisory. It does not establish policy.

The committee is working on two gas chromatography (GC) methods, tentatively called LUFT (Leaking Underground Fuel Tank) 1000 and LUFT 2000, for the determination of Volatile Range Organics (VRO) and Extractable Range Organics (ERO), respectively. The committee is also developing two gas chromatography/mass spectrometry (GC/MS) methods for volatile and extractable petroleum hydrocarbons. These four methods are intended to supersede existing California LUFT methods for characterizing petroleum contamination in the environment.

Two primary goals in adopting these methods are to improve data quality, and to reduce the uncertainty created by the various "modified 8015" — GC with a flame-ionization detector (FID) — Total Petroleum Hydrocarbon (TPH) methods being used. The variation of methods contributes to poor data comparability among laboratories.

At the same time, the committee wishes to encourage technical innovation and will recommend methods that are performance-based, rather than prescriptive. The intent is to move towards performance-based procedures with these new petroleum hydrocarbon

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methods. By doing so, the methods will be as flexible as possible, and suitable for the diverse data quality objectives in petroleum hydrocarbon investigations.

Until the new LUFT methods are issued, the committee is recommending guidance in two areas of concern regarding petroleum hydrocarbon analysis and data evaluation:

(1) quantitation ranges and product identification, and (2) cleanup of sample extracts to remove polar interferences.

Quantitation Ranges

The quantitation range for VRO is n-C6 to n-C12 (n-hexane to n-dodecane); the range for ERO is n-C10 to n-C28 (n-decane to n-octacosane). VRO and ERO are used to designate the ranges, instead of GRO (gasoline range organics) and DRO (diesel range organics), because other refinery products, such as jet fuel or Stoddard solvent, may wholly or partly elute in the same chromatographic range as fresh gasoline and diesel fuel; but it would be misleading to label them as such.

The laboratory should maintain a reference file of chromatograms of fresh, and weathered fuels and solvents — analyzed by the same method used for samples. If a comparison of the standard and sample chromatograms (“fingerprinting”) reveals a pattern match, this finding may be included in the lab report narrative. The quantitative data should, however, be reported as mg/L or mg/Kg, VRO or ERO. Laboratories should continue to use the appropriate analytical standards for calibration and quality control (refinery products such as gasoline and diesel, or n-alkane mixtures) for the analytical range(s) of interest.

Oxygenates are a special case: They will be included in the VRO result *if* they elute in the VRO retention time window; however, purging efficiencies and response factors are different for oxygenate and non-oxygenate hydrocarbons. Therefore, FID-VRO results should not be used to quantitate individual oxygenate compounds: GC/MS or GC with a photoionization detector (PID) are the preferred techniques. On most chromatography columns, MTBE will elute *before* the VRO range, and will not be included in the VRO result. The other oxygenates (TAME, DIPE, etc.) will generally elute in the VRO range.

The VRO and ERO ranges overlap (C10 - C12); the two results should not be combined to yield a “total” petroleum hydrocarbon result. The LUFT 2000 method will include, as an option, the determination of Heavy Extractable Range Organics (HERO) for residual petroleum products (e.g. motor oil) in the C28 - C40 range. Any deviation from these ranges should be explained in the laboratory report and, if appropriate, the project plan.

Extract Cleanup

Any organic compound will cause an FID response, and will be included in the petroleum hydrocarbon result derived from the total chromatographic peak area if it elutes in the GC retention time window (carbon range) defined by the method. Polar, biogenic compounds such as carboxylic acids can be significant interferences in hydrocarbon chromatography.

Solid-phase extraction (cleanup) using silica or alumina has been shown to be effective in removing these polar compounds, which may elute as components of an unresolved “hump” in the chromatogram. The amount of adsorbent required will depend on the amount of interferences and the activity of the adsorbent. More than one pass through a column or cartridge may be necessary. Batch extraction (adding adsorbent to the extract and mixing) is not as effective in removing interferences.

Some of these polar compounds may be degradation products of petroleum contamination. These compounds are excluded from measurement by extractable organics GC/FID methods (e.g. LUFT 2000) when silica or alumina cleanup of the extracts is performed. If the objective is to measure only *non-polar* compounds in the sample, cleanup should be done; if the objective is to measure *all* organic compounds, cleanup should *not* be done. A comparison of chromatograms of the same extract, with and without cleanup, may provide useful information on the composition of the sample.

Identification and quantitation of individual compounds in hydrocarbon GC/FID chromatography is unreliable; differentiation of polar petroleum degradation products and biogenic interferences is usually not possible. GC/MS is an alternative technique: it can provide an FID-like aggregate measure of organics (Total Ion Current), and identification of functional groups and compound classes. The ability of GC/MS to identify and quantitate individual compounds is compound and matrix dependent.

As the sampling and analysis plan is developed, and *before* samples are collected, the project managers and laboratories must understand, and agree upon, the intended uses of the data, and appropriateness and limitations of the methods.

The extractable organics cleanup procedure must be validated by the laboratory and documented as a Standard Operating Procedure (SOP) before samples are processed. The SOP should be referenced in the laboratory report and, if applicable, the project plan.

The laboratory is directed to SW-846, Update III (U.S. EPA Office of Solid Waste, Dec. 1996) Method 3600C, Section 8.0 for guidance on quality assurance and quality control (QA/QC). (SW-846 on-line: www.epa.gov/epaoswer/hazwaste/test/txmain.htm) At a minimum, the laboratory must demonstrate that compounds of interest are quantitatively recovered (Sec. 8.2). This demonstration should include:

- a) Initial demonstration of proficiency (Method 8000B, Sec. 8.4): recovery study using four replicates of a diesel standard spike in the matrix of interest.
- b) If an n-alkane standard is used to calibrate the instrument, a one-time check that each component of the standard is recovered quantitatively. The total area of the standard and the areas of individual compounds must meet the QC criteria established by the laboratory for daily continuing calibration checks. (Method 3600C, Sec. 8.3)
- c) Each batch of twenty or fewer samples should include a cleanup Laboratory Control Sample (LCS). The recoveries of the cleanup LCS, carried through all the extraction and analysis steps, and another LCS (prepared from the same standard) that is carried through all the steps except the cleanup are plotted separately on control charts. As data are accumulated, QC acceptance criteria for cleanup recovery precision and bias may be established by the laboratory.
- d) Associated QC samples, including method blanks, matrix spikes, and duplicates must be processed through the cleanup with the sample batch. (Method 3600C, Sec. 8.2) The concentration of the LCS and matrix spike is discussed in SW-846 Method 8000B, Secs. 8.5.1 and 8.5.2. The chromatographic pattern (elution order and relative peak area) must be unaffected by the cleanup.
- e) Surrogate compounds, such as fatty acids, for non-petroleum biogenic organics would be useful for measuring the effectiveness of the cleanup procedure at removing polar interferences, but at this time no surrogates are recommended.

If you have any questions or comments regarding this guidance letter, please contact Martin Snider at the Hazardous Materials Laboratory, tel. (510) 849-5258; fax (510) 540-2305; e-mail msnider@dtsc.ca.gov.

Sincerely,



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